Laser Ablation imaging with the icpTOF

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TOFWERK AG, Switzerland

contents

TOFWERK and the icpTOF

Instrument performance

LA imaging with the icpTOF: examples

Outlook

TOFWERK

A Global Provider of TOF Technology

- Company TOFWERK AG
- Headquarter Thun (Switzerland)
- Founded 2002
- Employees 57
- Products:
  - Custom instrumentation for research labs and and OEM partners
  - High performance end-user instruments

State-of-the-art performance in all environments

Zeppelin, Finland


Rainforest Manaus, Brazil


McMurdo Station, Antarctica

Based on the iCAP RQ

- Based on the ThermoScientific™ iCAP™ RQ ICP-MS
- Quadrupole based ICP-MS
- Market introduction
  - iCAP Q ICP-MS: 2012
  - iCAP RQ ICP-MS: 2016
- ICP-QMS with a small bench footprint

Compact vertical design.

QCell with unique flatapole design.

Zero user maintenance beyond the slide valve.

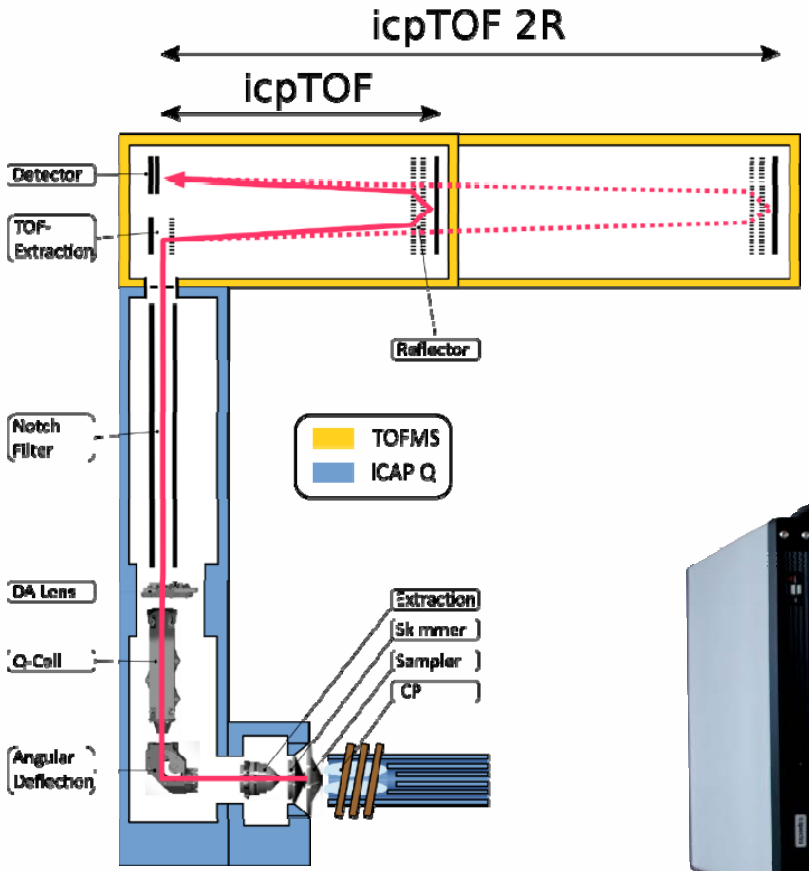
New solid state RF generator and all new electronics ensures stability and maximizes uptime.

Quick connect, self-aligning sample introduction system.

Drop-down door for simplified cone access.

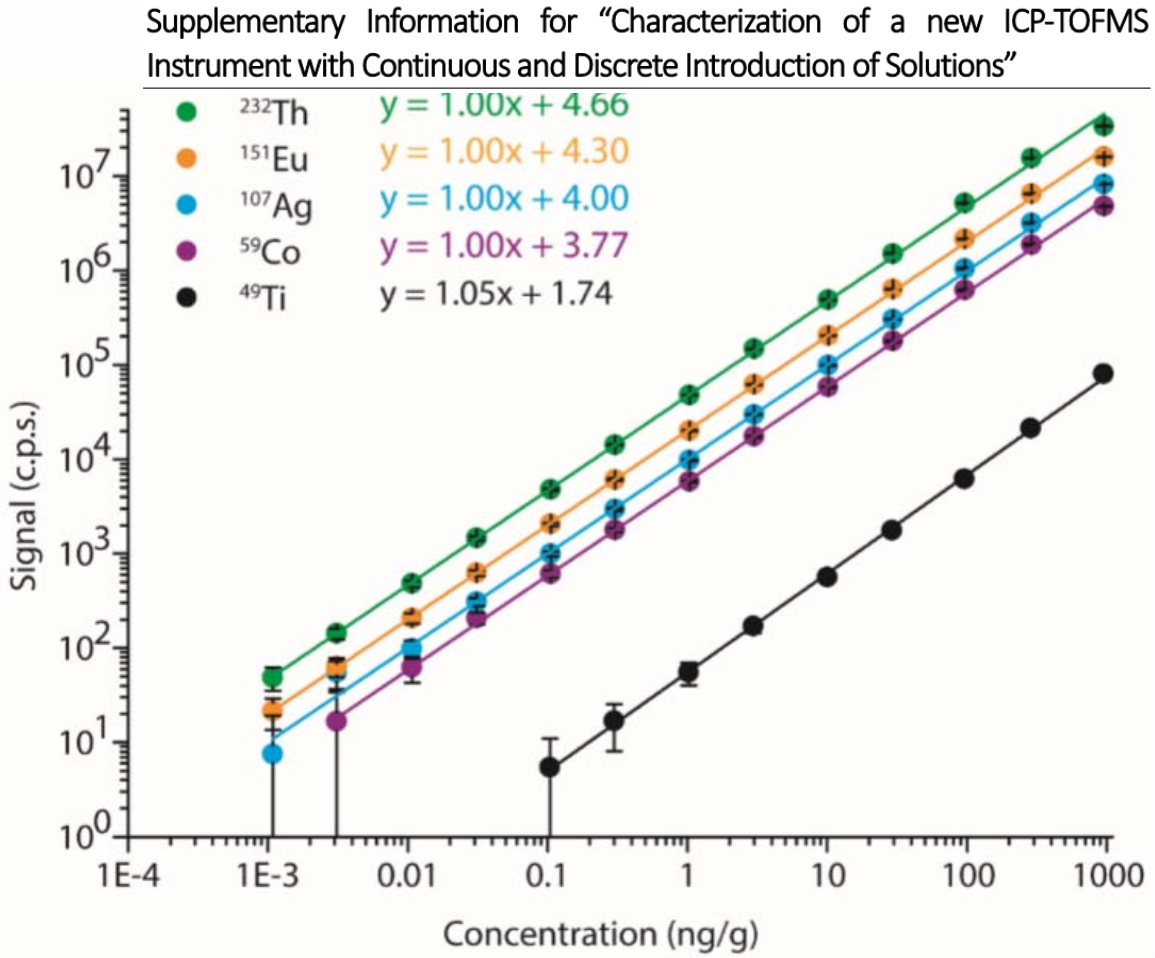
Instrument Layout

- TOFWERK
  - Notch filter
  - TOFMS
- iCAP RQ ICP-MS
  - ICP source
  - Water cooled interface
  - Primary ion optics
  - QCell



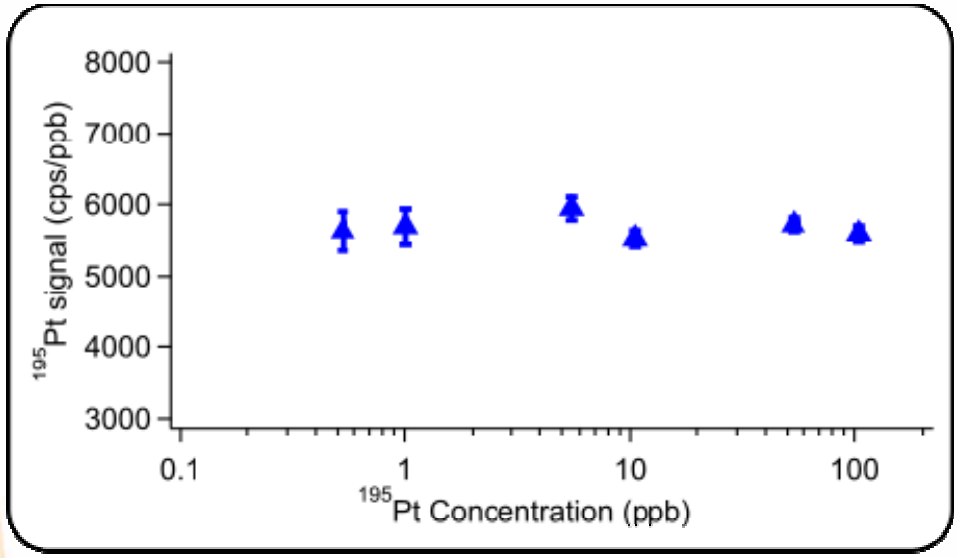
icpTOF Sensitivity

- Figure S1: Calibration curves for 49Ti, 59Co, 107Ag, 151Eu and 232Th obtained with the conventional pneumatic nebulizer and cyclonic spray chamber sample introduction system under standard acquisition mode (i.e. covering the mass range from 14N+ to 254UO+). The calibration for Th spans six orders of magnitude with detection saturation occurring at 1000 ng g-1.

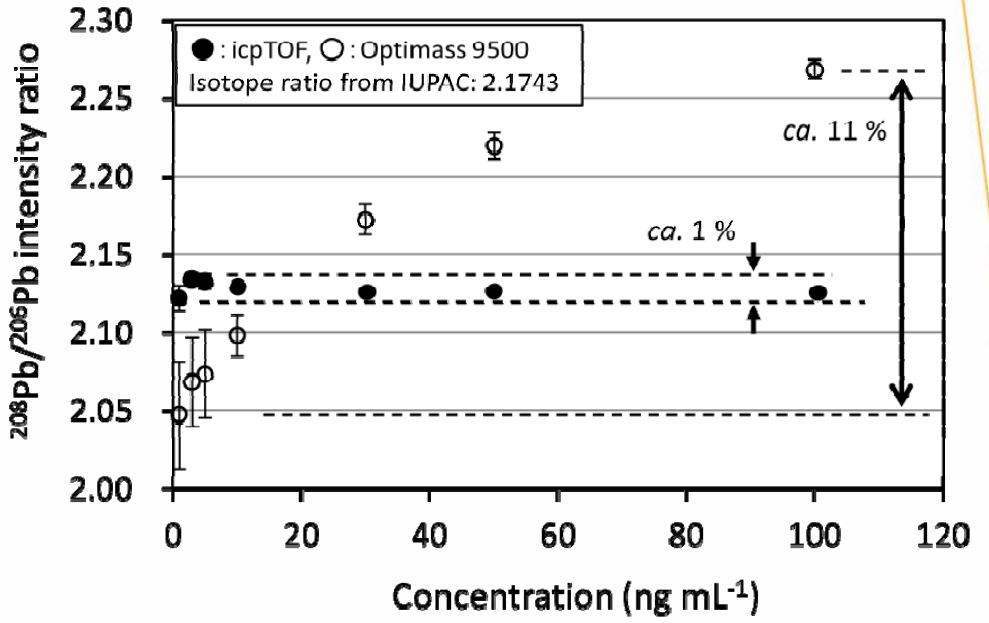


Linear Dynamic Range

- linear dynamic signal range



Hendriks et al., 2017, JAAS 32, p. 538

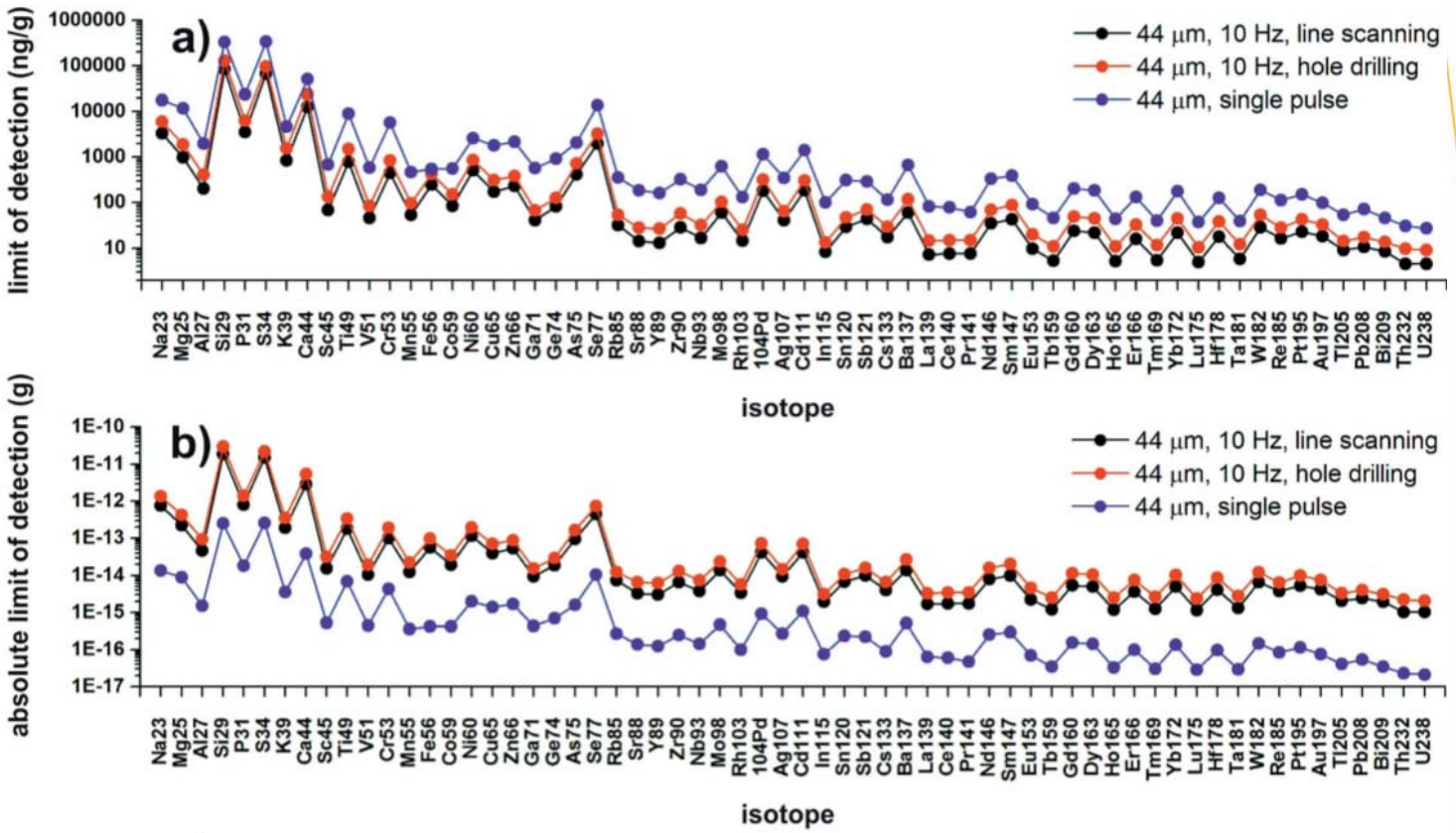


Ohata & Hagino, 2018, Int. J. Mass. Spec. 430, p. 31

icpTOF Performance

Fig. 1 (a) LODs for high-dispersion and low-dispersion LA using a 44 µm diameter laser spot.

(b) Absolute LODs calculated from data reported in (a).



Burger et al., 2017

TOFMS for Short Signals

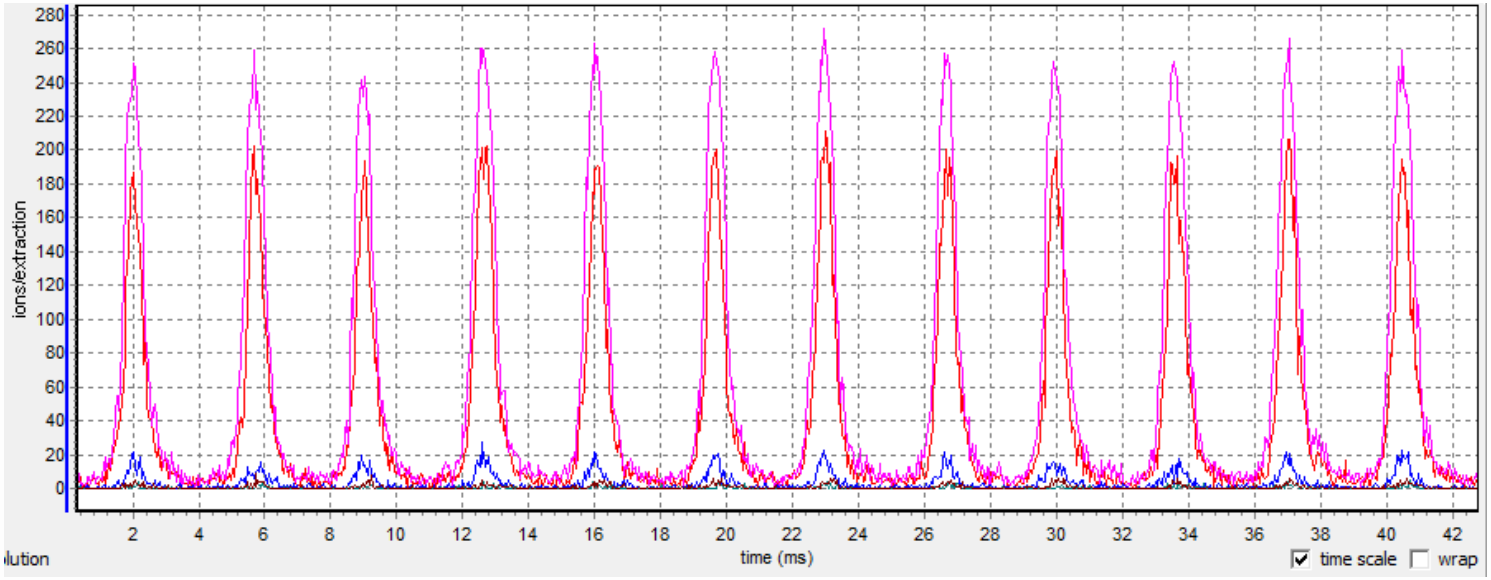
- 33’000 TOF extractions per second
- Example:

Laser ablation @

10 µm spot size

300 Hz

SRM NIST612



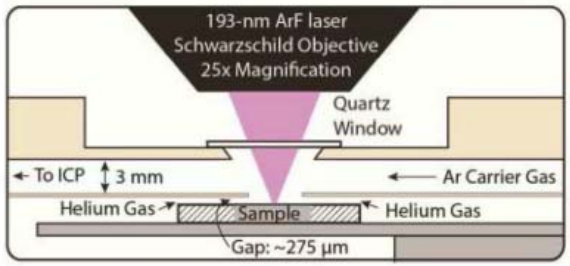
Analyte G2 with

Cobalt LA cell

- **Fully time resolved transient signals of individual laser shots**

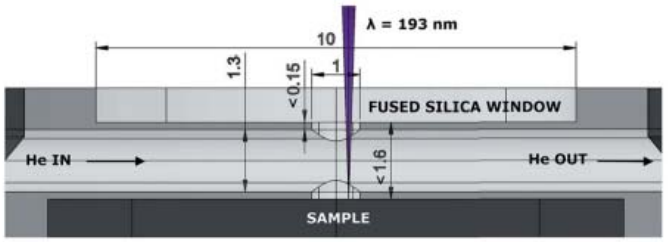
Laser Ablation Imaging

Fast tube cell, ETH Zürich



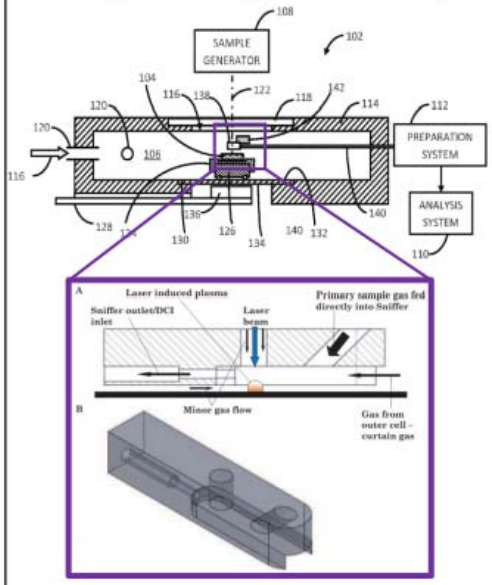
Wang *et al.*, Anal. Chem., 2013, 85 (21), pp 10107–10116
Gundlach-Graham *et al*. Anal. Chem., 2015, 87 (16), pp 8250–8258

Fast cell, Ghent University



Van Malderen *et al*. JAAS, 2015, 30, 119-125

Sniffer cell, Loughborough University

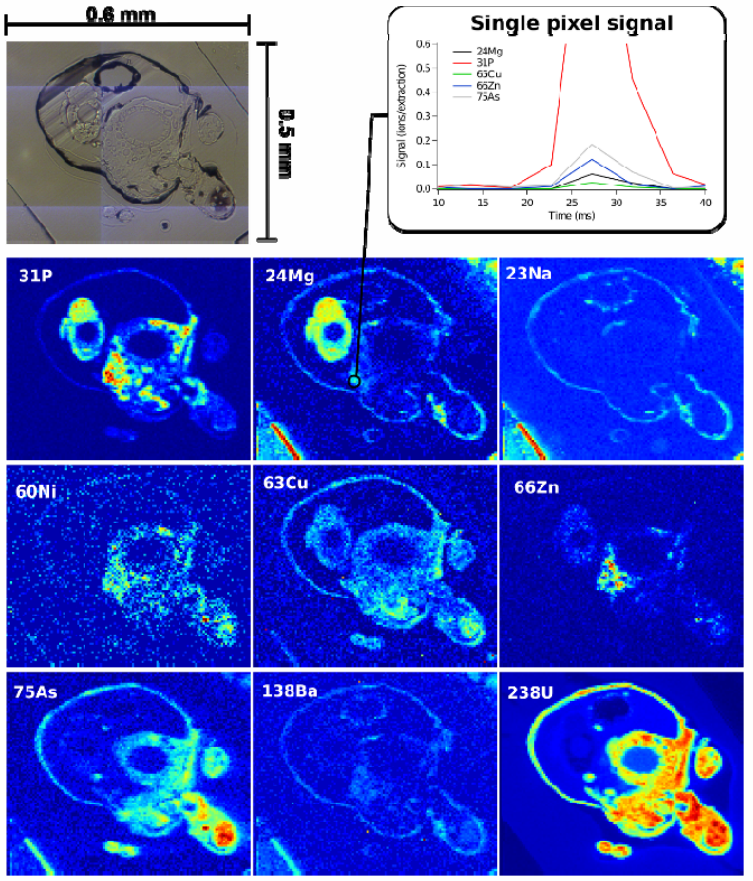


Douglas, Doctoral Thesis, 2013, Loughborough University
Sharp *et al.*, 2014, US Patent 0224775

- <<20 ms washout
- Increased spatial resolution
- Increased sensitivity
- Increased speed

Fast Imaging

- Each spot a complete Analysis
- Full mass spectra
- No Signal carry-over
- Example: Ceriodaphnia
  - 600x500 µm area
  - Laser: CETAC Analyte G2 with Helix Cell and ARIS
  - 5 µm spot size (12’000 pixels)
  - 20 Hz laser frequency
  - 100 µm/s scan speed
- **12 min analysis time**



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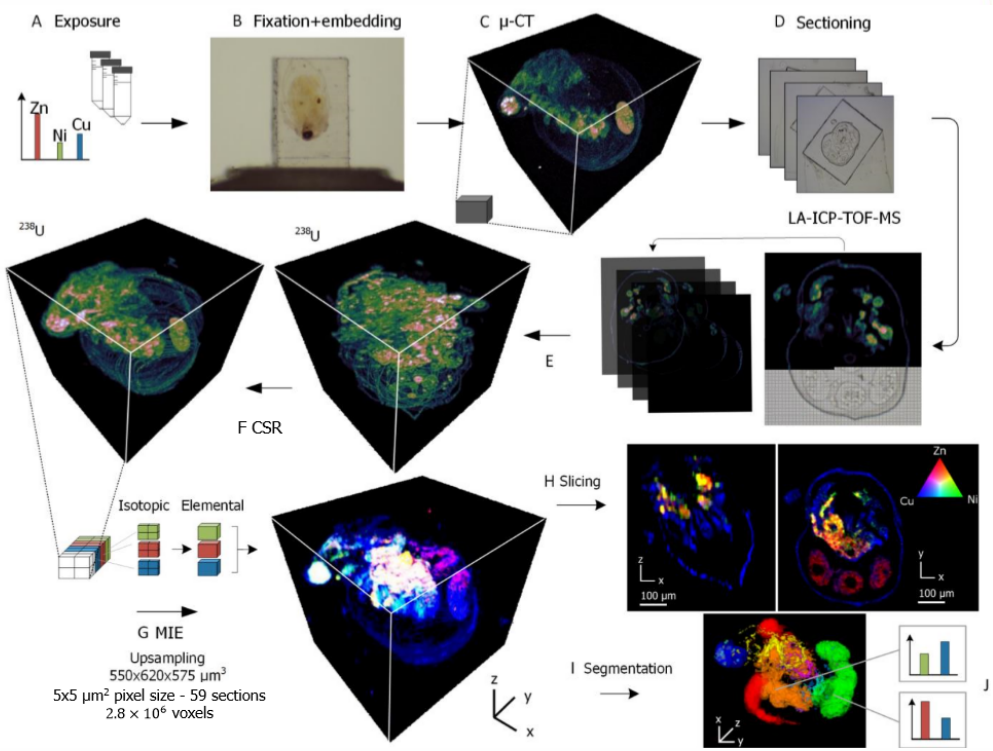
3D-Imaging

LA-ICP-MS

- Spot size: 5x5 µm
- 59 thin sections
- 2.8 x 10^6 voxels



analytical chemistry

Three-dimensional reconstruction of the tissue-specific multi-elemental distribution within Ceriodaphnia dubia via multimodal registration using laser ablation ICP-mass spectrometry and X-ray spectroscopic techniques

Stijn J. M. Van Malderen, Brecht Laforce, Thibaut Van Acker, Charlotte Nys, Maarten De Rijcke, Riet De Rycke, Michiel De Bruyne, Matthieu Boone, Karel A.C. De Schamphelaere, Olga Borovinskaya, Björn De Samber, Laszlo Vincze, and Frank Vanhaecke

Anal. Chem., Just Accepted Manuscript
DOI: 10.1021/acs.analchem.7b00111
Publication Date (Web): March 3, 2017

Van Malderen et al., 2017

Collaboration: Group of Frank Vanhaecke, Uni Gent

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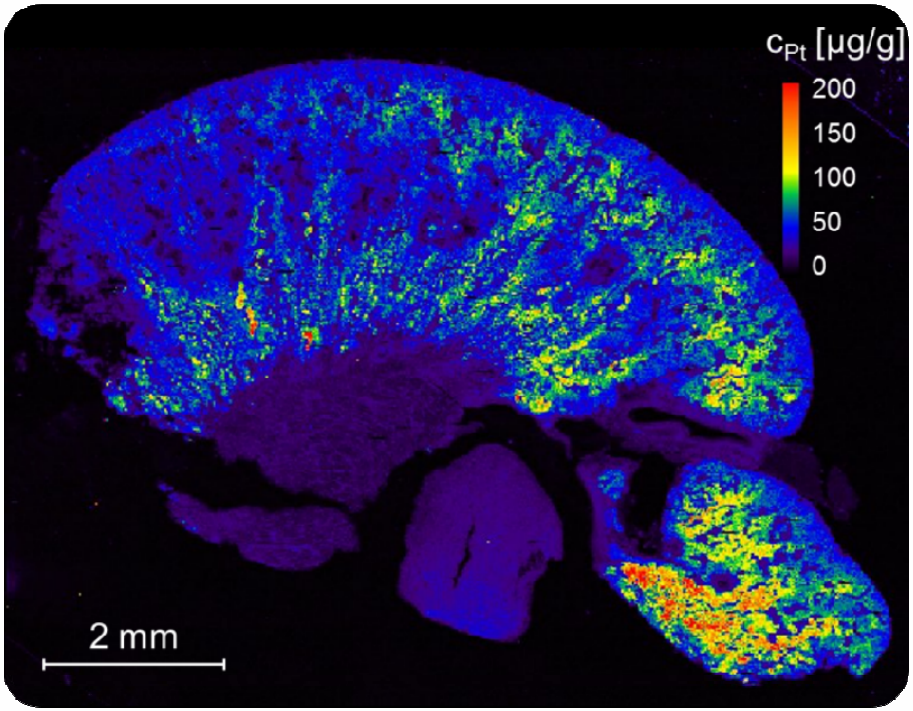
Bio-Imaging

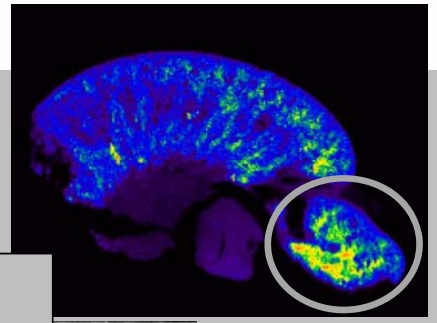
- **Sample**
  - Rat kidney
  - After Cis-Pt treatment
- **Experimental**
  - Laser: Analyte G2 193 nm
  - Aerosol Rapid Introduction System (ARIS)
  - Rep.rate: 100 Hz
  - Spot size: 20 µm
  - Scan speed: 10 pixels/s, 200 µm/s
  - **Quantification with element standards embedded in Technovit**



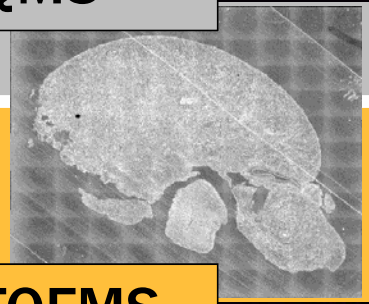
Collaboration: Group of Uwe Karst, Uni Munster

Imaging: TOF vs. Quad

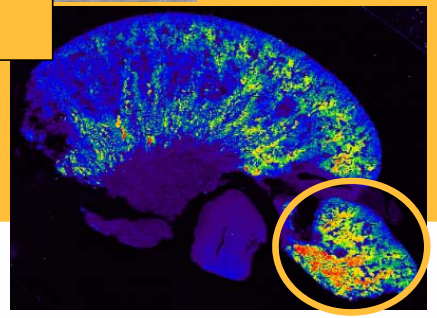
- **QMS**
  - Spot size: **50 µm**,
  - Scan speed: **100 µm/s**
  - 3 Analytes
- **TOFMS**
  - Spot size: **20 µm**,
  - Scan speed: **200 µm/s**
  - **Full mass spectra**
  - **Higher pixel resolution**



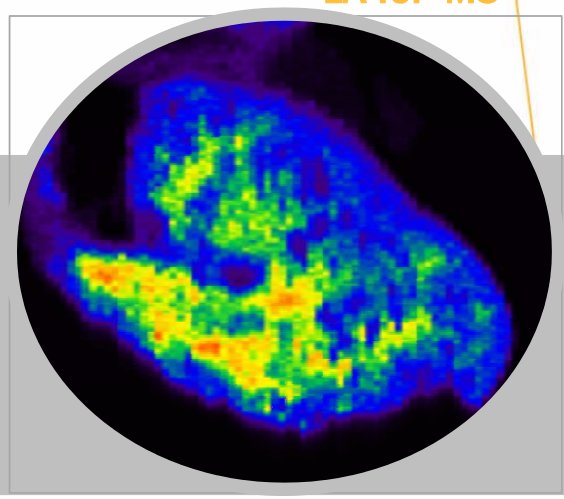
QMS

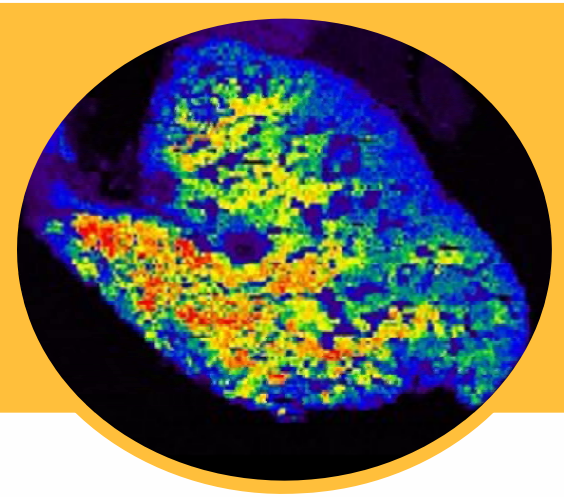


TOFMS



LA-ICP-MS





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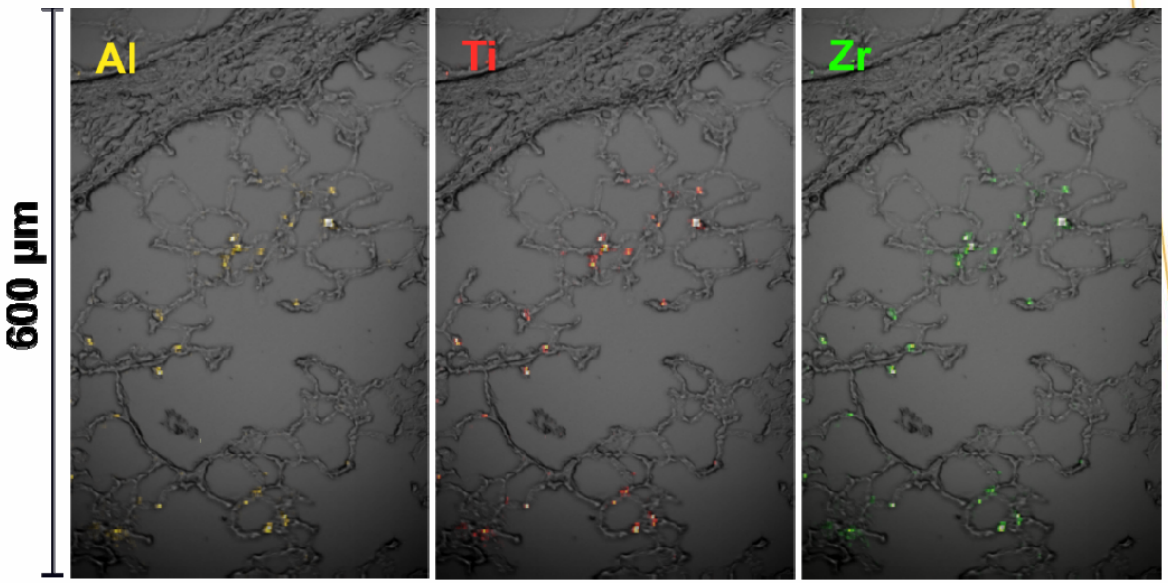
Imaging and Particles

- **Sample**
  - Rat lung instilled with a mixture of Al2O3, TiO2, and ZrO2 NPs (46 nm)
  - Quantification with gelatin standards
- **Laser**
  - NWR213, ESI NewWave
  - Laser energy 0.5 J/cm2
  - 5x5 µm laser spot size
  - Line scans
- **Precise localization and quantification of particles in tissue sample**

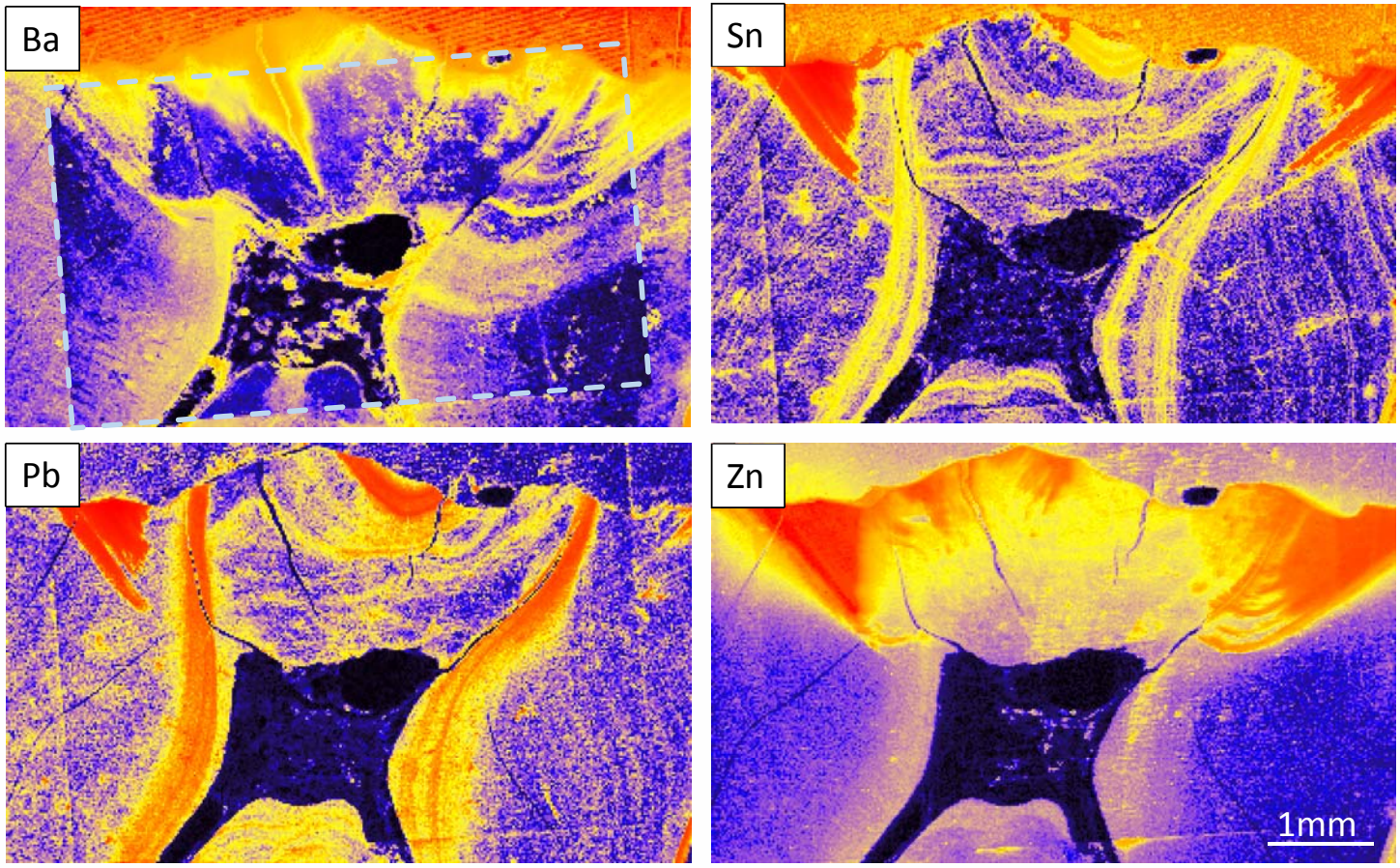


Collaboration: Group of Uwe Karst, Uni Munster

Biomaterials: human tooth

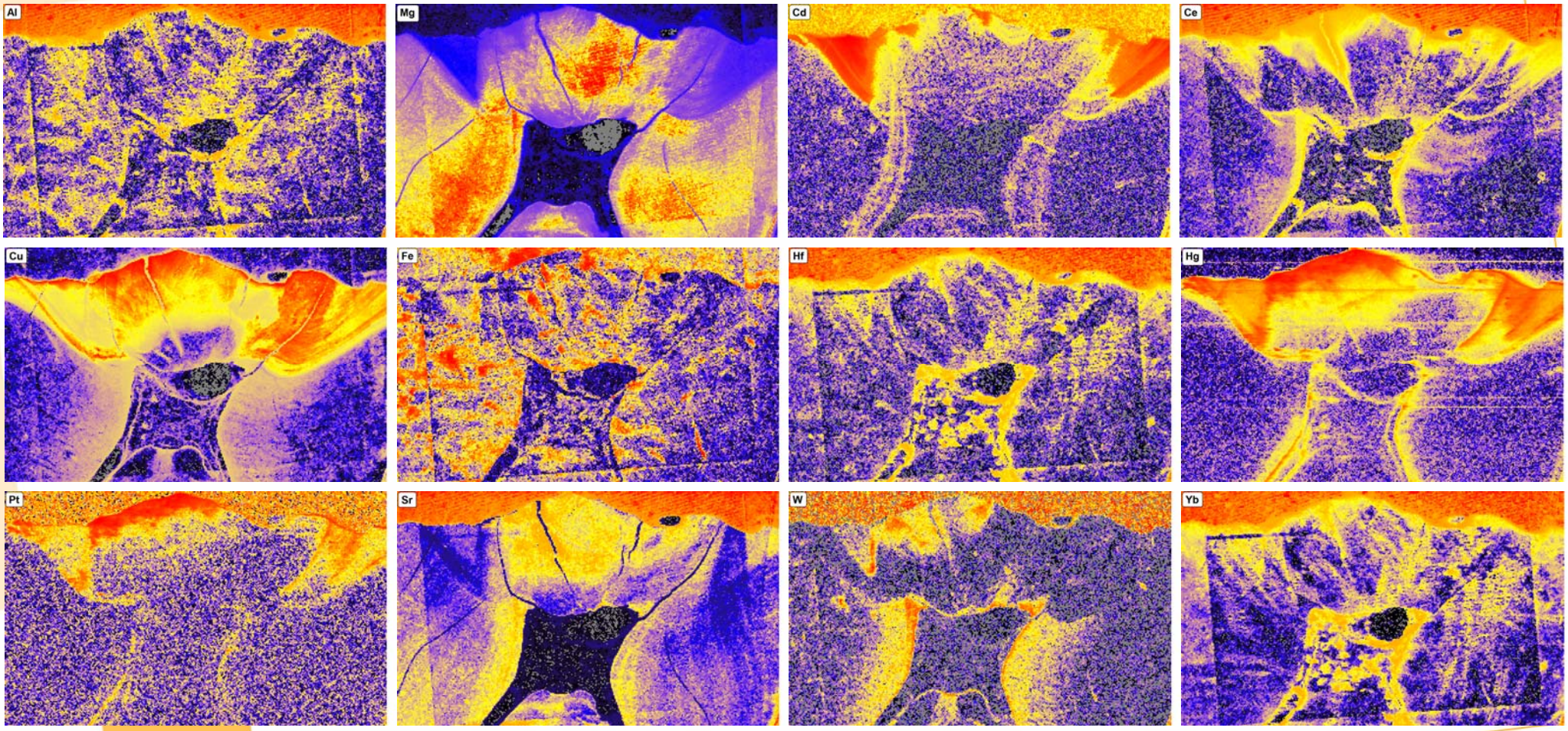
Element distribution in human tooth shows growth patterns, exposure to environmental factors during growth

- 20 µm at 20 Hz
- 325 x 199 pixel
- 1h 10 min acquisition
- Analyte G2 + ARIS



London Metallomics Facility, sample from Peter Pilecki – King's College London

Biomaterials: human tooth



Element mapping

Example: Garnet

Fe-Mg-K map (R-G-B band)

Micashist from the South Carpathians, Romania*

Teledyne CETAC Analyte G2 + Cobalt cell

Dosage 1 (laser shots / pixel)

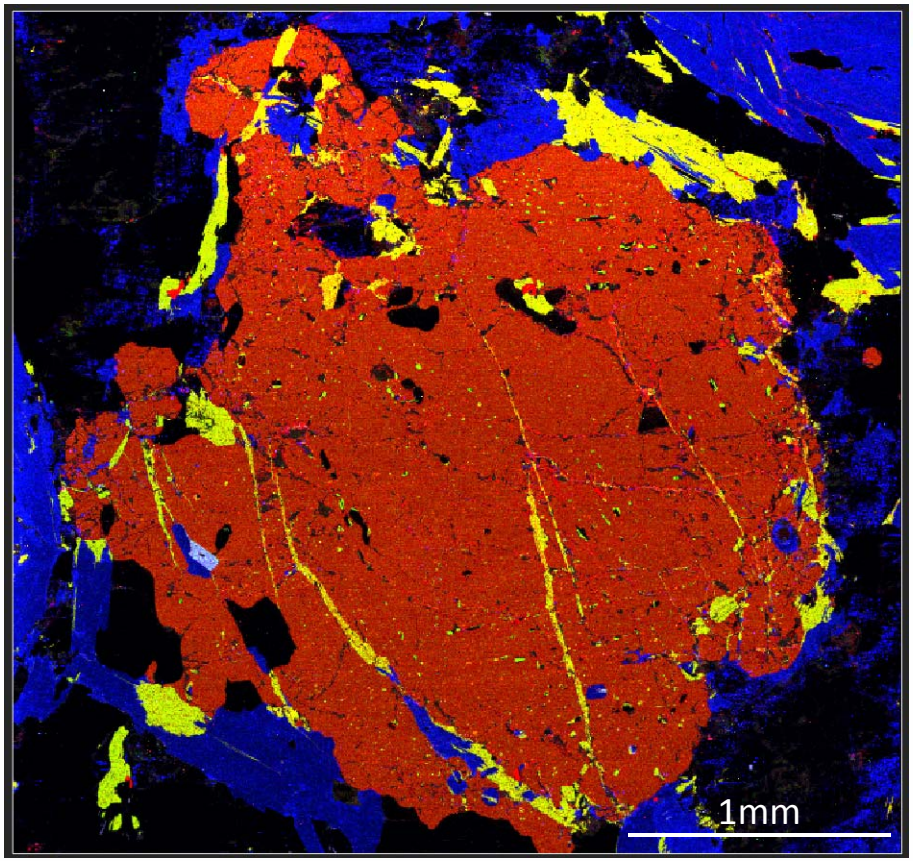
Data processing in HDIP (Teledyne)

5 µm spot size

150 Hz

410 kpixel

acquired in ~2 h

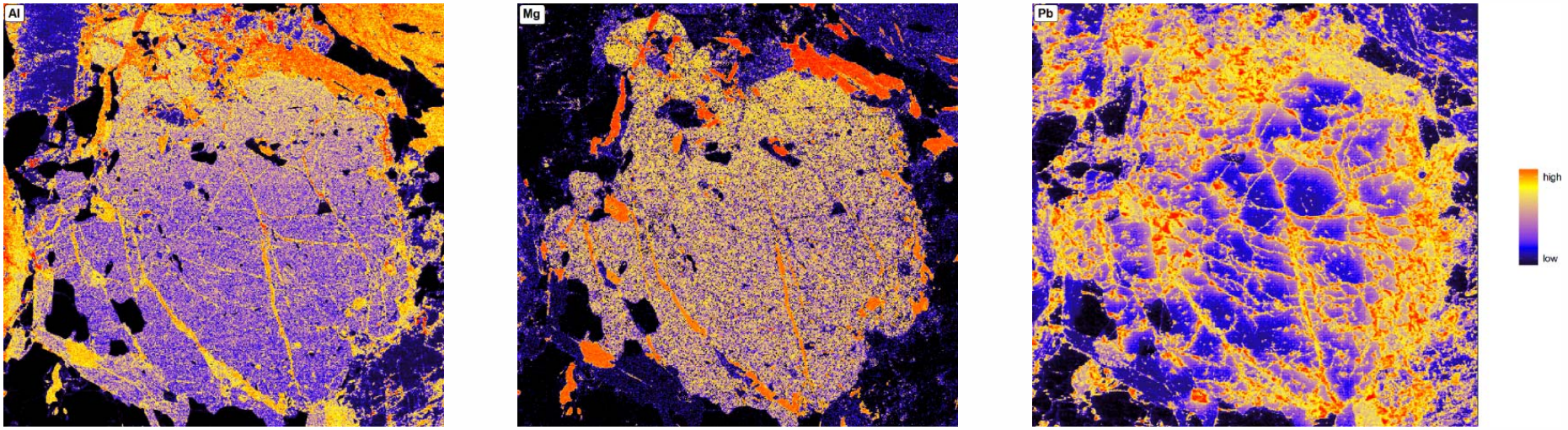


*sample courtesy of Gavril Săbău, Geological Institute of Romania

Element mapping

Example: Garnet

Major and accessory elements

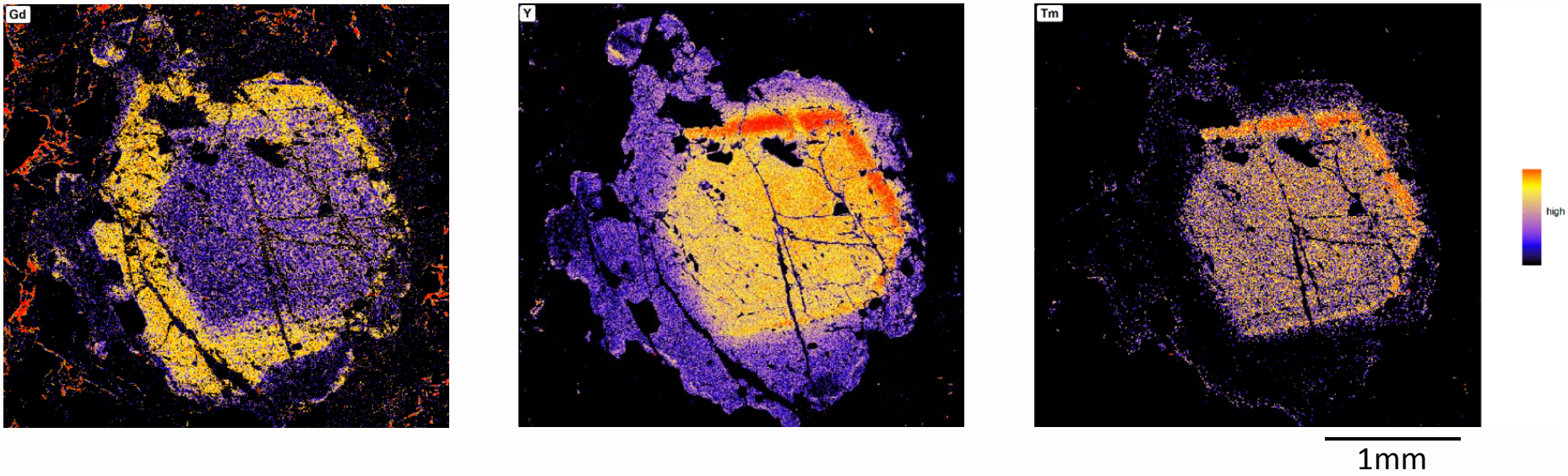


Overlay maps of all measured isotopes of each element, weighted by isotopic abundance.
Data processing in R, using TOFWERK library to access HDF5 analysis data.

Element mapping

Example: Garnet

Major elements



Overlay maps of all measured isotopes of each element, weighted by isotopic abundance.
Data processing in R, using TOFWERK library to access HDF5 analysis data.

Element mapping

Example: Peridotite

Melt formation and element mobility

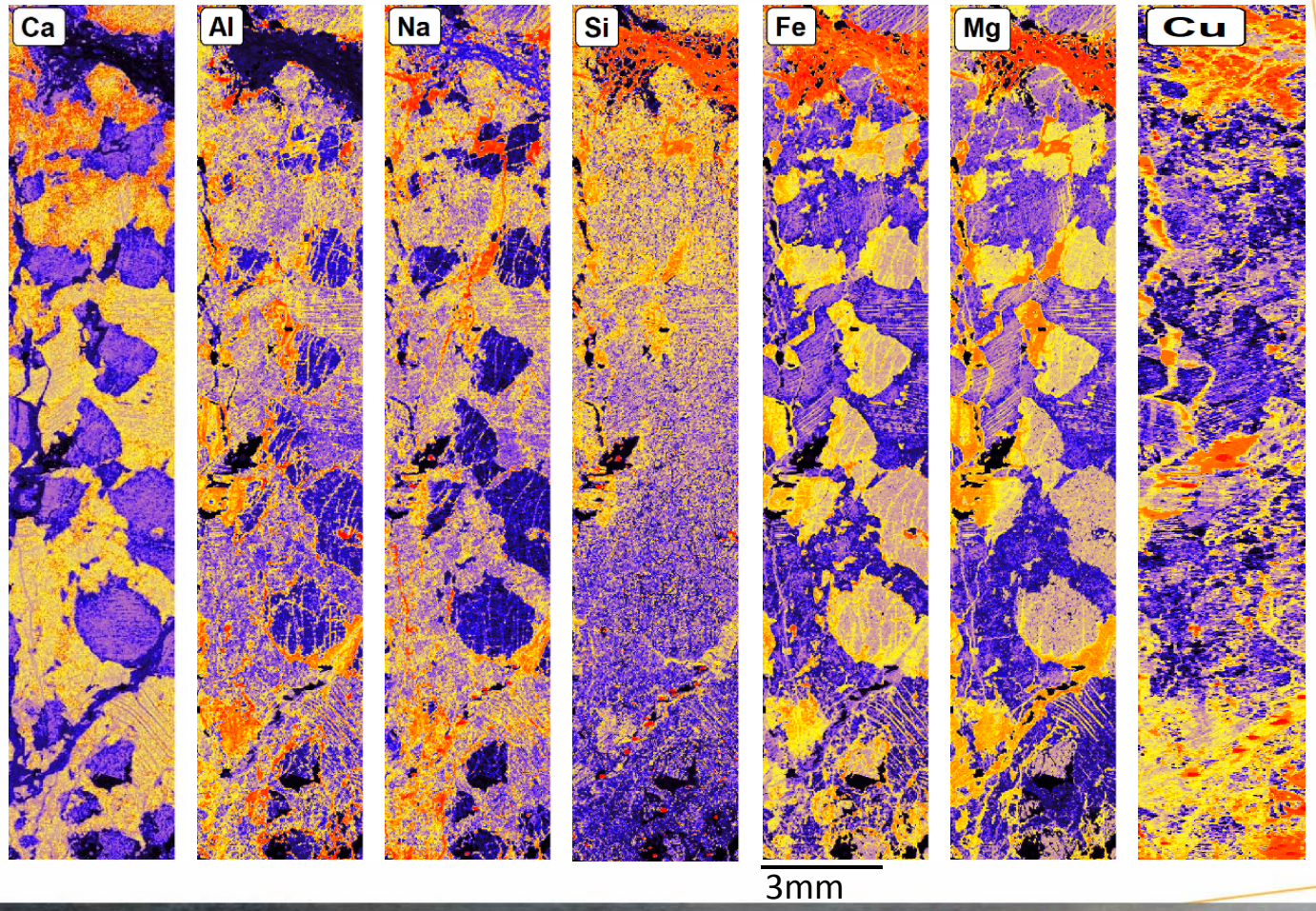
Analyte G2 + ARIS

20 µm spot size @ 30 Hz

194 x 1000 pixel

acquisition time 3 h

Overlay maps of all measured isotopes of each element, weighted by isotopic abundance.
Data processing in R, using TOFWERK library to access HDF5 analysis data.
Sample curtesy of Yannick Bussweiler, Uni. Münster.



Element mapping

Example: Peridotite

Melt formation and element mobility

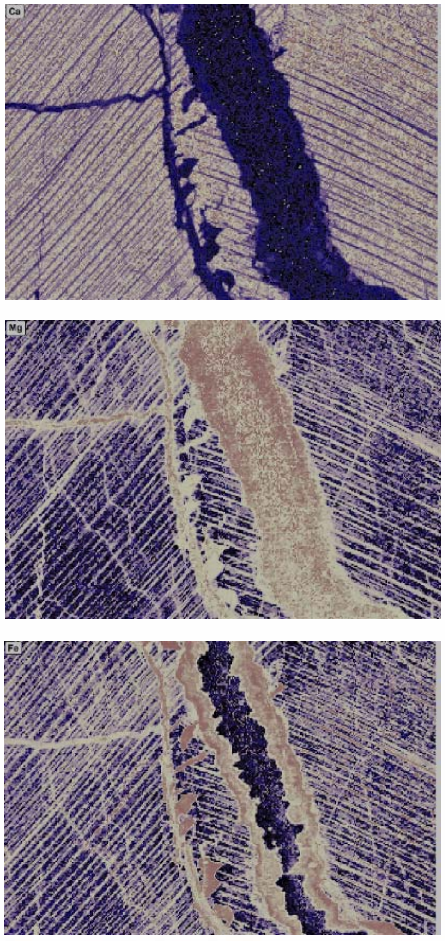
Analyte G2 + ARIS

10 µm spot size @ 30 Hz

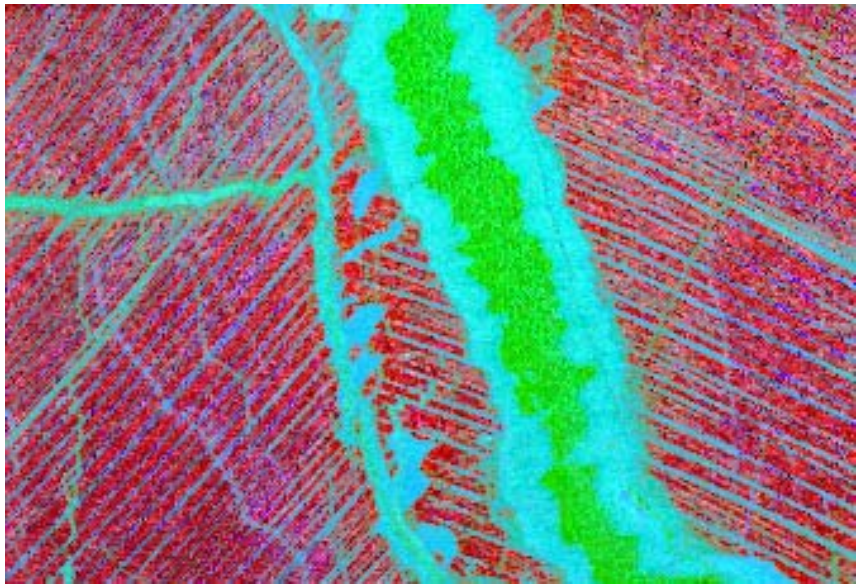
336 x 229 pixel

acquisition <1 h

Overlay maps of all measured isotopes of each element, weighted by isotopic abundance.
Data processing in R, using TOFWERK library to access HDF5 analysis data.
Sample curtesy of Yannick Bussweiler, Uni. Münster.



Combined Ca-Mg-Fe (RGB) map

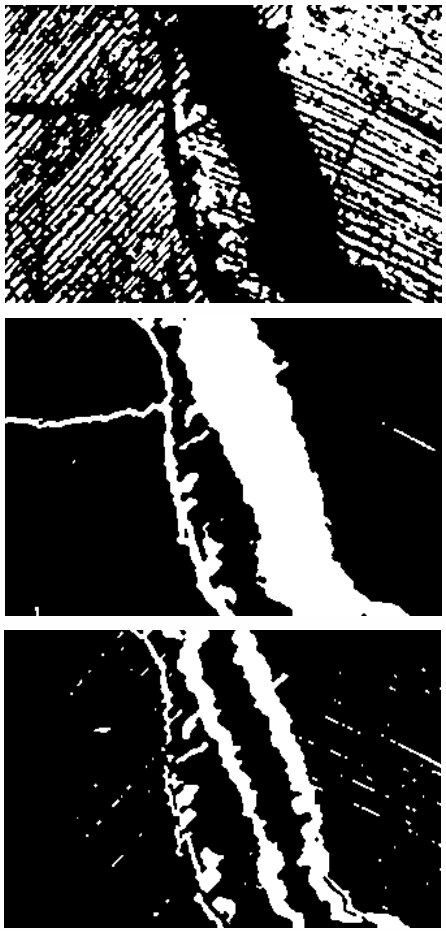


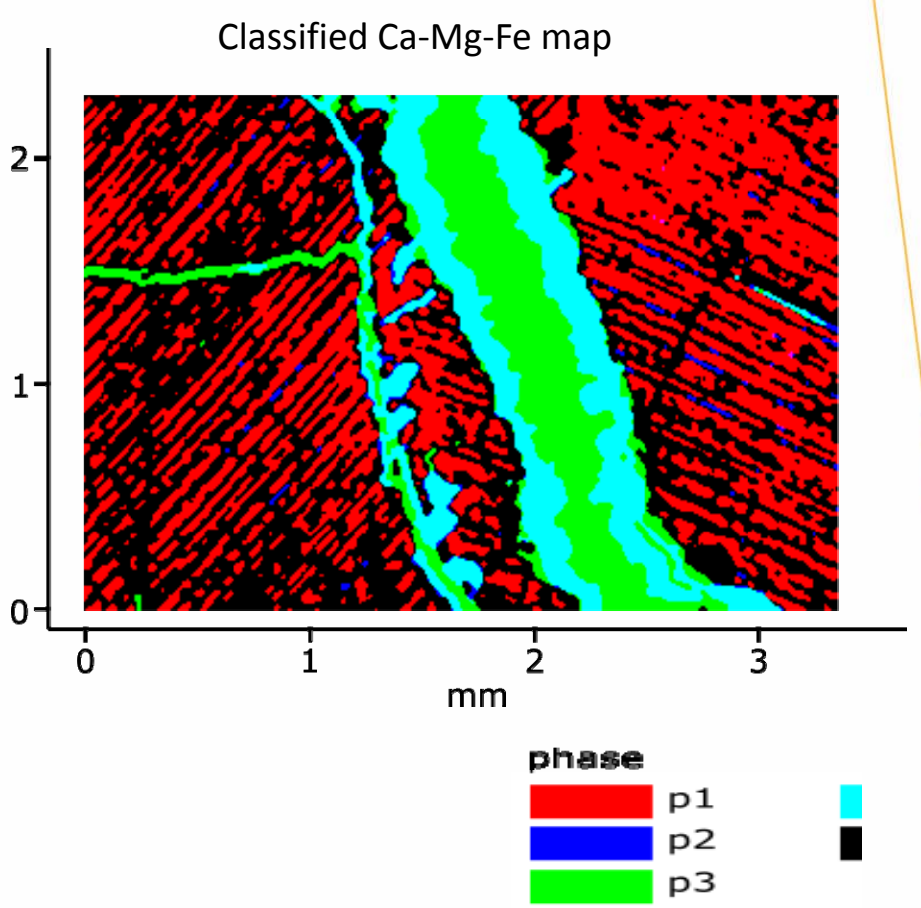
1mm

Element mapping

Example: Peridotite

Mineral phase classification

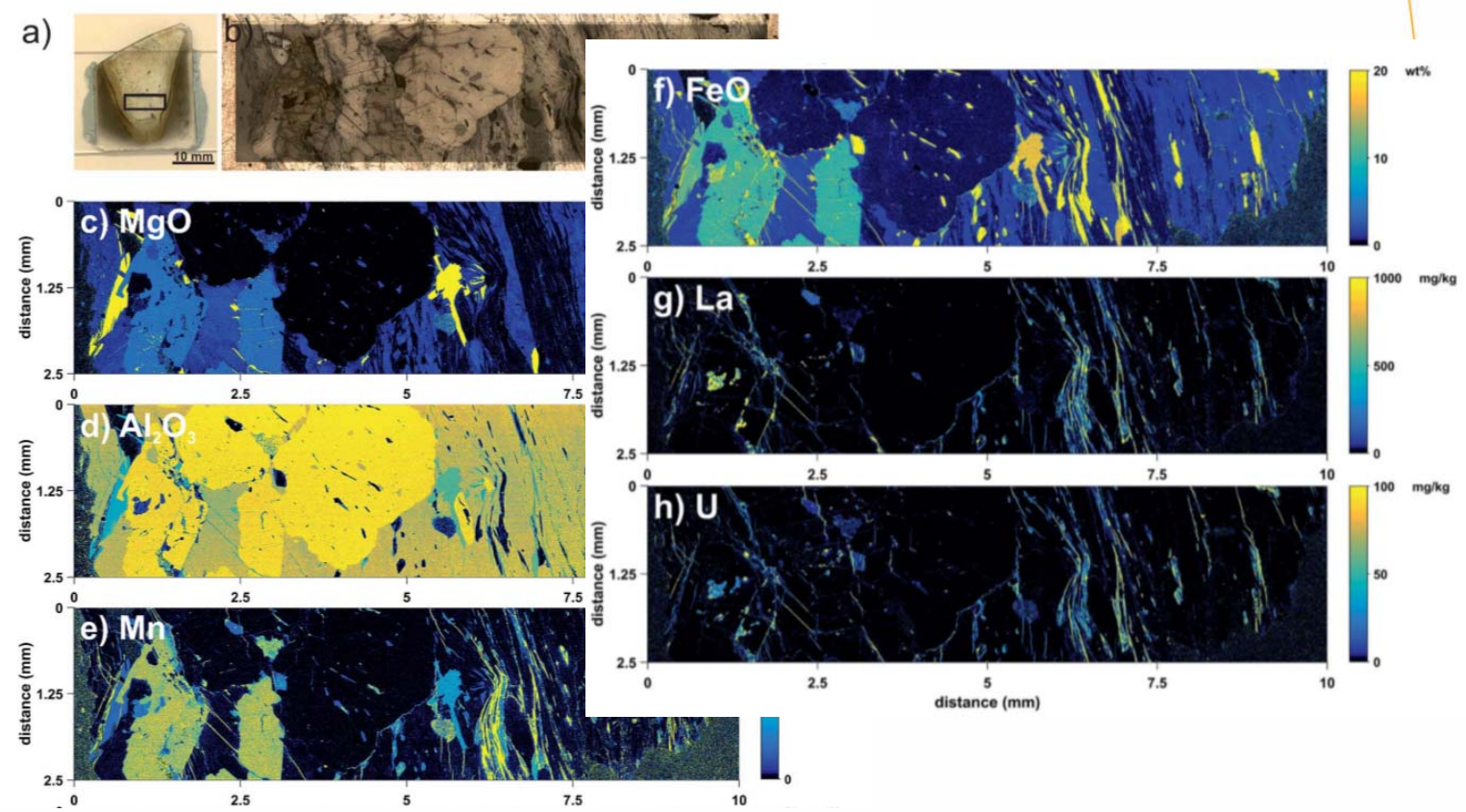




Data processing in R, using TOFWERK library to access HDF5 analysis data. Sample curtesy of Yannick Bussweiler, Uni. Münster.

Element mapping

Fig. 3 (a) Multi-phase geological thin section HC101523, imaged area is highlighted by a black frame, (b) post-ablation microscope image of the sampled region, (c–h) selection of quantitative elemental images. Concentrations are reported either as weight percentage of oxide or mg of pure element per kg of sample.



Burger et al., 2017

Current developments

Laser manufacturers work on fast and ultra-fast wash-out LA cells

→ '1 Megapixel per hour' and beyond (1 kHz laser frequency)

Software:

optimisation for high-speed imaging

instant visualisation

data-driven acquisition

user-friendly, high-performance data analysis

Thanks to:

- University Ghent
- University Münster
- ETH Zürich
- Teledyne CETAC
- ESI NewWave
- Iolite Software
- London Metallomics Facility, King's College London
- Thermo Fisher Scientific

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